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MERCURY BROMIDE RECONSTITUTION IN THE HGBR LASER SYSTEM 1/1

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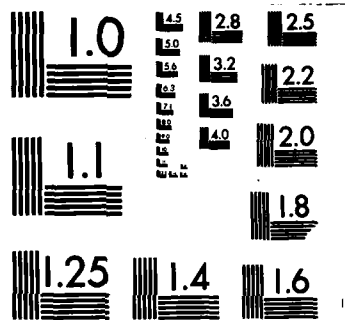
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HgBr LASER SYSTEM

C. S. Liu

Final Report Covering
May 15, 1983 to June 15, 1984

Contract No. N00014-83-C-0375
Office of Naval Research

September 11, 1984

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I. INTRODUCTION

This report summarizes research work performed at the Westinghouse R&D Center under Contract No. N0014-83-C-0375 for the period between May 15, 1983, and June 15, 1984. The major effort was to perform experimental life studies of an UV pre-ionized HgBr laser and reconstitute the reaction products such as Hg and Hg₂Br₂. *mercury bromide*

During past years, we had conducted extensive experimental lifetime studies of a small scale HgBr laser. From these experiments, we selected suitable materials¹ for laser construction, developed procedures to fabricate and fill the laser tube, and finally, we lifetested^{2,3} the laser for over 5×10^6 shots. Those results indicate that pinhole-free gold plated nickel is chemically inert to the HgBr₂ discharge and can be used for constructing long-lived high prf HgBr lasers. However, for a large system it is difficult to plate the base metal with pinhole free gold. It is this motivation for developing a HgBr₂ recovery system.

In this report, we describe the construction of a long-lived, high prf HgBr laser with a built-in HgBr₂ reconstitution system and present experimental test data which confirm our theoretical predictions. Finally we recommend the future design of a practical 10^{10} shots HgBr laser.

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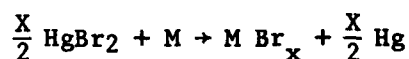
II. CHEMICAL REACTIONS IN HgBr LASERS

The chemical reactions taking place in an HgBr laser is quite similar to that of commercial metal halide lamps. During the laser discharge, electron impact dissociates and excites the HgBr_2 and then the dissociated species recombine with one another to reform HgBr_2 . In principle, these dissociation and re-association processes can go on forever, providing the re-association rate is fast enough to recovery all the fragments and there is no loss of mercury or bromine due to chemical reactions with other metals such as electrode materials. The most important rule one should keep in mind when selecting materials is that the metal bromide of the metals used in the laser should be much less stable than that of the HgBr_2 at the laser operating temperature. In this way, the metal used will not rob the bromine or Hg from HgBr_2 molecules. The bromine cycle will be kept within the HgBr_2 system itself. Thus, the HgBr laser can have a long operating life. For this to be valid, the device must be made under well controlled, clean conditions so that impurities such as oxygen do not enter the cycle and change the course of reactions.

The typical operating temperature of an HgBr laser is between 150 and 200°C. It is important to use materials in the laser tube which are chemically inert to HgBr_2 , HgBr , Hg , Br and Br_2 at such temperatures. In selecting materials, simple thermochemical calculations are useful to eliminate the unsuitable materials, but these calculations are not sufficiently adequate to predict the chemical stability of the materials chosen because they do not include non-equilibrium conditions, nor take into account the excited state chemistry, chemical transport reactions and photochemical or ionic effects occurring in laser discharges. The ultimate means in selecting the materials of the HgBr laser is experimental chemical compatibility study. Nevertheless, thermodynamic

calculations can eliminate many candidates and thus reduce the experimental effort to a manageable level.

Glasses, quartz and ceramic oxides are inert to HgBr_2 , HgBr , Hg , Br and Br_2 under thermodynamic equilibrium conditions, thus they can be used as HgBr laser tube as insulator materials. Polyamides are also inert to the HgBr_2 gas when they are shielded from UV radiation and corona. For metals, the tendency of reactions with HgBr_2 , HgBr , Hg , Br and Br_2 can be predicted by calculating the free energy change for each of the participating compounds. Table 1 lists the free energy changes⁴ for the chemical reactions of



where M is the metal to be used in HgBr lasers. Al, Cr, Ni, Ta and Ti have negative values of free energy change; therefore, they are definitely not suitable for HgBr lasers. Since the free energy change for Mo, W, Au, Pt or Re has a large positive value, the metal- HgBr_2 reaction is negligible. For instance, if one has chosen tungsten as a base metal to build a HgBr laser operated at 500°K , the free energy change, ΔF , for the reaction $5/2 \text{HgBr}_2 + \text{W} \rightarrow \text{W Br}_5 + 5/2 \text{Hg}$ is 56,000 calories. The equilibrium constant, K, can be calculated as follows:

$$K = \exp \left(- \frac{\Delta F}{RT} \right) = 3 \times 10^{-24}$$

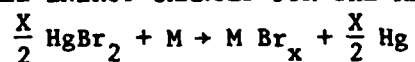
The equilibrium constant, K, is defined as

$$K = \frac{(P_{\text{WBr}_5}) \cdot (P_{\text{Hg}})^{5/2}}{(P_{\text{HgBr}_2})^{5/2}}$$

Since $P_{\text{HgBr}_5} = 0.1 \text{ atm (at } 500^\circ\text{K)}$ ⁵ we calculate

Table 1

THE FREE ENERGY CHANGES FOR THE REACTIONS



<u>M</u>	<u>M Br_x</u>	<u>ΔF 500°K (kcal)</u>
Al	AlBr ₃	-65
Au	AuBr ₃ (AuBr, AuBr ₂)	+53 (+17, +37.1)
C	CBr ₄	+49.4
Cr	CrBr ₂ (CrBr ₃)	-29.5 (-26)
Mo	MoBr ₅ (MoBr ₄ , MoBr ₃ , MoBr ₂)	+54 (+40, +26, +13)
Ni	NiBr ₂	-7.5
Pt	PtBr ₄ (PtBr ₃ , PtBr ₂ , PtBr)	+54 (+41.5, 27, 13)
Re	ReBr ₃	+38.3
Ta	TaBr ₅	-37
Ti	TiBr ₄ (TiBr ₃ , TiBr ₂)	-64 (-66, -50)
W	WBr ₅ (WBr ₆ , WBr ₄ , WBr ₂)	+56 (+88, +50, +23)

$$[P_{\text{WBr}_5}] \cdot [P_{\text{Hg}}]^{5/2} = 9.5 \times 10^{-27}$$

Since $P_{\text{WBr}_5} \approx 0.01$ atm (at 500°K) the equilibrium pressure of Hg is

$$P_{\text{Hg}}|_{\text{eq}} \approx 2.5 \times 10^{-10} \text{ atm}$$

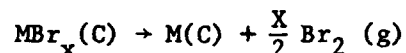
As the free-energy change for tungsten and HgBr_2 reaction is positive, 56,000 calories, the tungsten reduction of HgBr_2 will be negligible. The thermodynamic equilibrium calculations indicate that as soon as the partial vapor pressure of Hg or HgBr_2 reaches $\sim 2.5 \times 10^{-10}$ atm at 500°K, all the chemical reactions of HgBr_2 and tungsten will cease. However, in the case of using Ni as the material for a HgBr laser, the free-energy change, ΔF , of the chemical reaction of $\text{Ni} + \text{HgBr}_2 \rightarrow \text{NiBr}_2 + \text{Hg}$ is negative 7,500 calories. The equilibrium constant, K , is

$$K = 1.9 \times 10^3$$

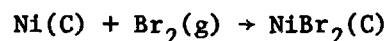
The equilibrium pressure of Hg is calculated to be 1.9×10^2 atm in order to stop the chemical reaction. Since the vapor pressure of Hg at 500°K is only about 0.06 atm⁶ (and cannot reach 2×10^2 atm), the chemical reaction of HgBr_2 and Ni will proceed indefinitely until all the HgBr_2 is totally reduced by the nickel. Therefore, nickel is not a suitable metal for use in HgBr lasers.

Near the electrode region, chemical reactions become more complicated. There will be present HgBr_2 , HgBr , Hg and free bromine. Since HgBr is less stable than HgBr_2 , any metal which is inert to HgBr_2 should also be inert to HgBr . One concern when using noble metals is that they have a tendency to amalgamate with Hg, which may cause severe problems. The amalgamation of Hg can quickly deplete the Hg from HgBr_2 as well as reduce the mechanical strength of the material used. Because the Hg-Br chemical bond is stronger than that of Hg-X (where X - Au, Pt, Re), the free bromine breaks down the Hg-X alloy bond to form HgBr_2 and prevents

the formation of the Hg-X. However, if one loses bromine from the HgBr₂ in the laser tube by other reactions then excess mercury will be tied up with Au or Pt. Unfortunately, free bromine reacts with almost any metal in contact with it at 500°K. From the equilibrium constants of the reactions



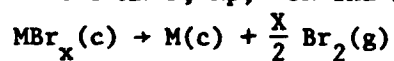
one can predict the direction in which the reaction proceed under certain conditions. The equilibrium constants and the equilibrium pressures of Br₂ for the above reactions are listed in Table 2.⁴ The thermodynamic calculations for NiBr₂ indicates that even if the partial vapor pressure of Br₂ is as low as 7.2×10^{-17} atm, the reaction still proceeds toward left, in the above equation, namely:



In the case of gold, until the partial vapor pressure of Br₂ reaches 3.83 atm (at 500°K), the reaction will proceed quickly toward right. That is, the AuBr₃ will continuously dissociate into Au and Br₂ until the bromine reaches its equilibrium pressure of 3.83 atm. In the HgBr laser, the free bromine pressure will only reach 10^{-4} to 10^{-5} atm. Therefore as far as bromine reaction is concerned, gold is excellent, platinum and rhenium are good, molybdenum and tungsten are questionable and nickel is not suitable for the HgBr laser system.

There are metals in which the reaction produces a protective film on the surface to retard further reaction (passivation). Thus, materials such as Ni, Al and stainless steel can sometimes be used even though the thermodynamics are unfavorable. However, such metals can only be used as the container material, not as the electrode since the discharge will readily destroy the protective coating.

Table 2

EQUILIBRIUM CONSTANTS, K_p , FOR THE REACTIONS

MBr_x	$K_p(500^\circ K)$	P_{Br_2} equilibrium
$AuBr_3$	$P_{Br_2}^{1.5} = 7.5$	3.83 atm
CBr_4	$P_{Br_2}^2 = 10^{6.7}$	2321 atm
$MoBr_5$	$P_{Br_2}^{2.5} = 2.8 \times 10^{-14}$	3.8×10^{-6} atm
$NiBr_2$	$P_{Ni} = 7.2 \times 10^{-19}$	7.2×10^{-19} atm
$PtBr_4$	$P_{Pt}^2 = 7.6 \times 10^{-7}$	8.7×10^{-4} atm
$ReBr_3$	$P_{Re}^{1.5} = 2.8 \times 10^{-6}$	2×10^{-4} atm
WBr_5	$P_{Br_2}^{2.5} = 2.1 \times 10^{-13}$	8.5×10^{-6} atm

After a careful analysis one can conclude that the metal used for electrodes should be either gold or platinum, metals used near the laser discharge could be gold or platinum plated nickel and metals situated far away from the electrodes could be even relaxed to Mo, W or stainless steel. However, one must always keep in mind that no matter what materials he is going to use, a vacuum tight ultra-clean system is the key to the long-lived HgBr laser. The required cleanliness and chemical inertness is difficult to achieve in practice.

III. HgBr₂ RECONSTITUTION SYSTEM

In a HgBr laser, the discharge pulse dissociatively excites the HgBr₂ generating various free radicals such as HgBr(B), HgBr(X), Br Br₂, Hg*, Hg, etc. Between the discharge pulses, they will recombine with one another to reform the HgBr₂. The rate of the association is a function of temperature, temperature distribution, vapor density, buffer gas pressure, current density, gas flow rate and geometry. For a continuously pulsed laser, a steady state condition will be established and each species will maintain a certain equilibrium pressure. If the metals used in the laser tube are not totally inert, there will be a continuous buildup of Hg and HgBr vapors, causing a gradual deterioration of laser performance. The ultimate remedy is to provide a bromine source which can react with the Hg and HgBr vapor to reconstitute the HgBr₂. It is obvious that one cannot use free bromine because of its uncontrollable high vapor pressure at the laser operating temperature which not only affects the discharge but also absorbs laser photons. However, some metal bromides having very low vapor pressure at the laser operating temperature can be used as a bromine source. If the metal bromide used is less stable in comparison to the HgBr₂ then the free Hg will grab the bromine from the metal bromide to form HgBr₂ and leave the metal precipitate in the recovery chamber. Therefore two major criteria in selecting the metal bromide for the reconstitution process are (1) very low vapor pressure at the laser operating temperature and (2) chemically less stable in comparison with the HgBr₂. Figure 1 shows a schematic diagram of the HgBr₂ reconstitution system for the HgBr laser. A high speed blower in the laser chamber provides gas circulation fast enough for high pulse repetition rate operation. From a separate, low throughput, flow loop, the gas is pumped out through a reconstitution chamber which contains the desired metal bromide. The operating conditions

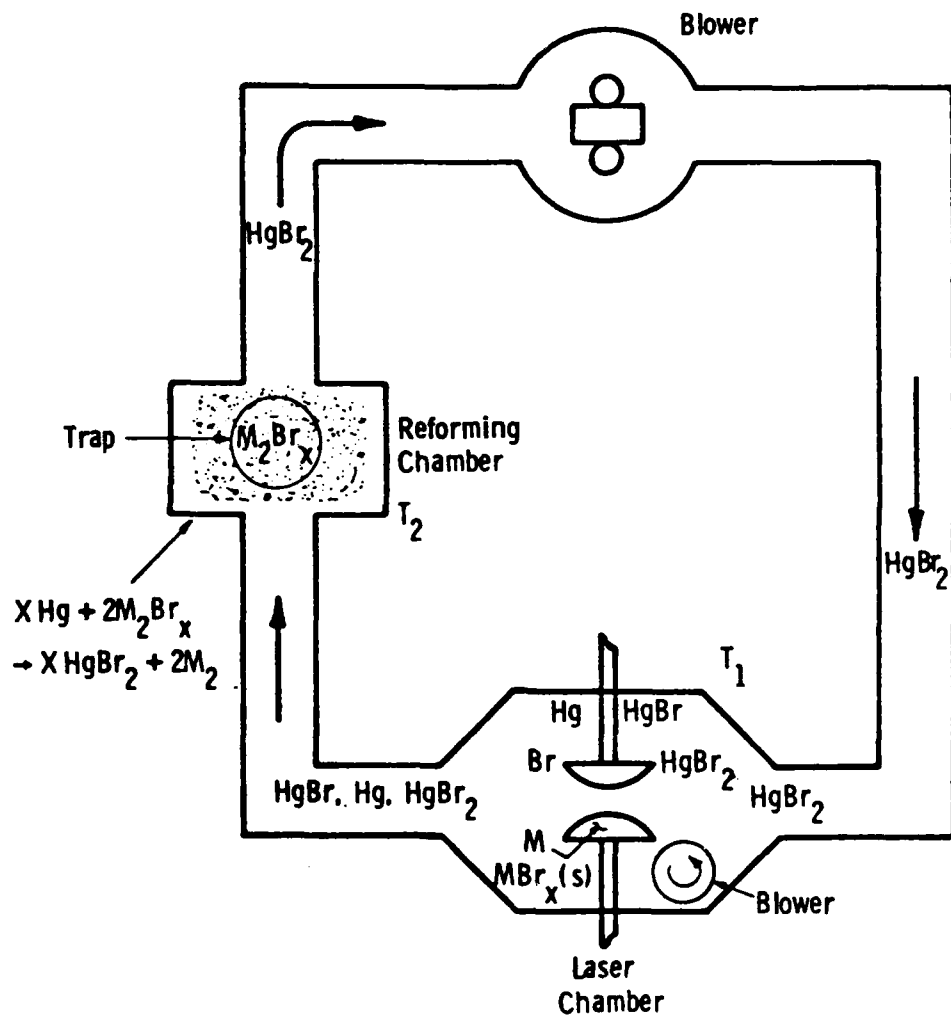
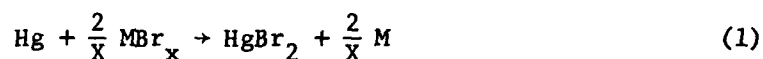
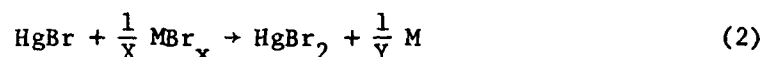


Figure 1 Mercuric Halide Recovery System
(Not to scale)

of the reconstitution system, such as temperature and flow rate, are optimized according to the rates of the following chemical reactions:



and



Since the reconstitution process takes place under local thermodynamic equilibrium conditions, the thermochemical calculations are valid in this region. Table 3⁴ lists the possible candidates for the HgBr_2 reconstitution according to their thermodynamic data. Column A indicates the type of bromides used, and column B and C indicate the free energy changes for reaction 1 and reaction 2, respectively. The free energy values in columns B and C are the measures of the tendency

Table 3
Possible Candidates for the HgBr_2 Reconstitution Process

Bromide	ΔF for	ΔF for
	$\text{Hg} + \frac{2}{X} \text{MBr}_X = \text{HgBr}_2 + \frac{2}{X} \text{M}$ (in cal)	$\text{HgBr} + \frac{1}{X} \text{MBr}_X = \text{HgBr}_2 + \frac{1}{X} \text{M}$ (in cal)
ReBr ₃	-26,000	-13,400
MoBr ₂	-13,000	- 7,000
MoBr ₃	-17,400	- 9,100
MoBr ₄	-20,000	-10,400
MoBr ₅	-21,600	-11,200
WBr ₂	-23,000	-11,900
WBr ₄	-25,000	-12,900
WBr ₅	-22,400	-11,600
PtBr ₂	-27,000	-13,500

for the reactions to proceed under the stipulated conditions. Large negative value of ΔF means that the reconstitution process will proceed rapidly. Among these bromides, only MoBr_2 and WBr_5 are readily available. Therefore, our reconstitution tests were limited to these two bromides. Figure 2 shows the free energy changes of reactions as a function of temperature calculated from the thermodynamic data. The reconstitution rates increase with increasing temperature. However, the operating temperature is limited by the vapor pressure and the chemical stability of the bromide used. The upper limit of the operating temperature of a reconstitution system using WBr_5 or MoBr_2 is set by its vapor pressure (no more than 10^{-4} atm) and it is 410°K for WBr_5 or 600°K for MoBr_2 respectively. A simple HgBr_2 reconstitution test setup is shown in Figure 3. In the first experiment, we conducted a test without any reconstitution agent in the tube. One end of a U-shaped tube with HgBr_2 and clean Ni foil in it was heated to 200°C. As soon as the HgBr_2 started to vaporize, the bright metallic Ni foil turned to a yellow dull color due to the formation of NiBr_2 on the surface. At the cooler end of the U-shaped tube we collected HgBr_2 , Hg_2Br_2 and Hg but no NiBr_2 or Ni. Then we performed similar tests with MoBr_2 or WBr_5 powder in the tube for the purpose of reconstitution. At 200°C, both MoBr_2 and WBr_5 worked very effectively. Neither Hg nor Hg_2Br_2 were detected in the cold zone. Since WBr_5 had ~ 1 torr vapor pressure at 200°C, small amounts of WBr_5 powder were condensed near the cold spot. In a practical system, the MoBr_2 is much preferred to the WBr_5 because of its low vaporization.

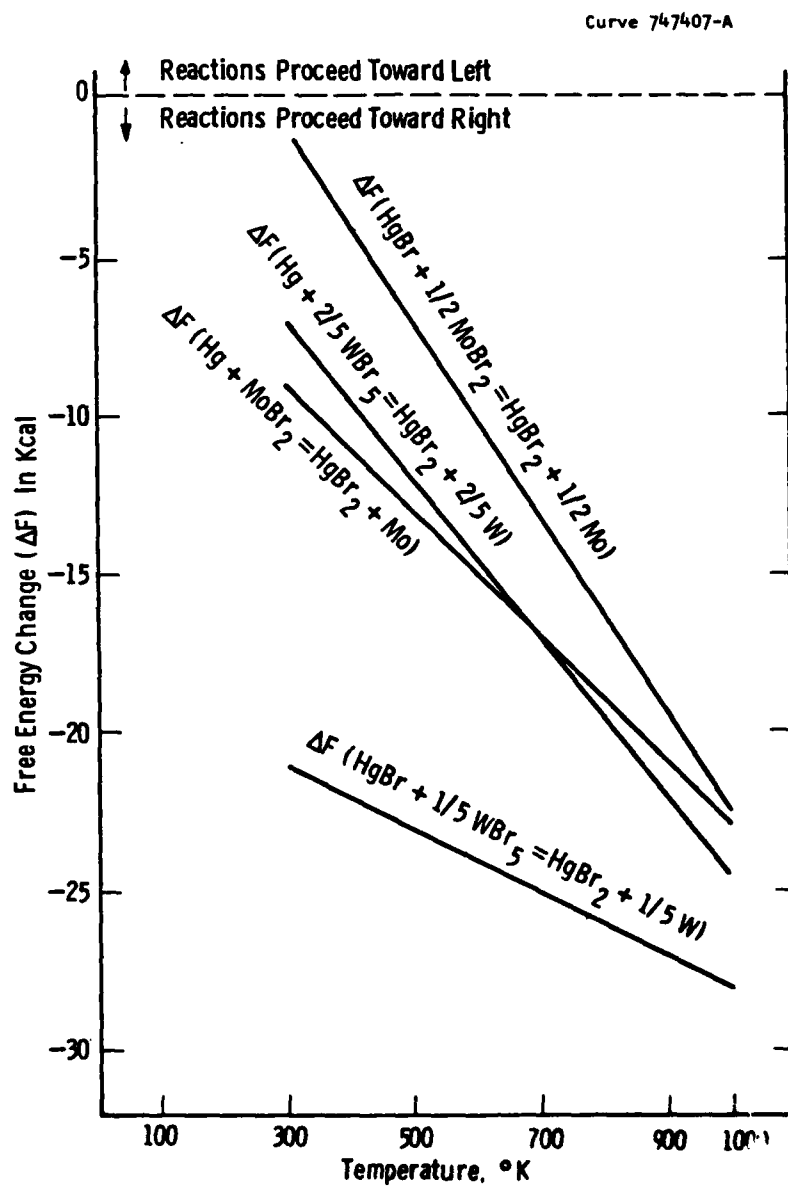


Figure 2 Free Energy Change, ΔF , as a Function of Temperature

Figure 3 Simple HgBr₂ Reconstitution Test

IV. HgBr LASER LIFE TEST

The high PrF sealed-off HgBr laser with a HgBr_2 reconstitution system is shown in Figure 4. The laser tube was fabricated from a six-inch glass pipe with two #304 stainless steel end plates. The electrode supporting structures and gas circulating blower were made of gold-plated nickel. The front surfaces of the electrodes were capped with 5 mil gold foil. The UV preionization was generated from an array of sparks formed by platinum wires. The discharge gases which consist of ~ 10 Torr of HgBr_2 vapor, 100 Torr of N_2 and 900 Torr of neon flowed through two parallel electrodes with the aid of a squirrel cage blower.

From previous HgBr_2 discharge tests², we observed high loss rates of gold and platinum from the main electrodes and UV preionizers which made us aware of potential problems resulting from metallic coating of optics. In this laser tube, we inserted two glass baffles to confine the gas circulation which significantly reduced the possibility of the coating the optical windows.

The laser gas is pumped out from one of the end plates through a HgBr_2 reconstitution chamber which contains MoBr_2 powder. The operating temperature and flow rate of the reconstitution chamber are pre-optimized according to the thermodynamic equilibrium calculations. The entire experiment was conducted at a pulse repetition rate of 50 Hz. The input energy was stored in four 2,700 pf ceramic capacitors charged to 10 kV through a L-C inversion circuitry. The energy was discharged through grounded grid EG&G 3202 thyratrons. During the test, a vacuum photo-diode was used to monitor the laser output. The laser discharge fluorescence without lasing was also periodically measured.

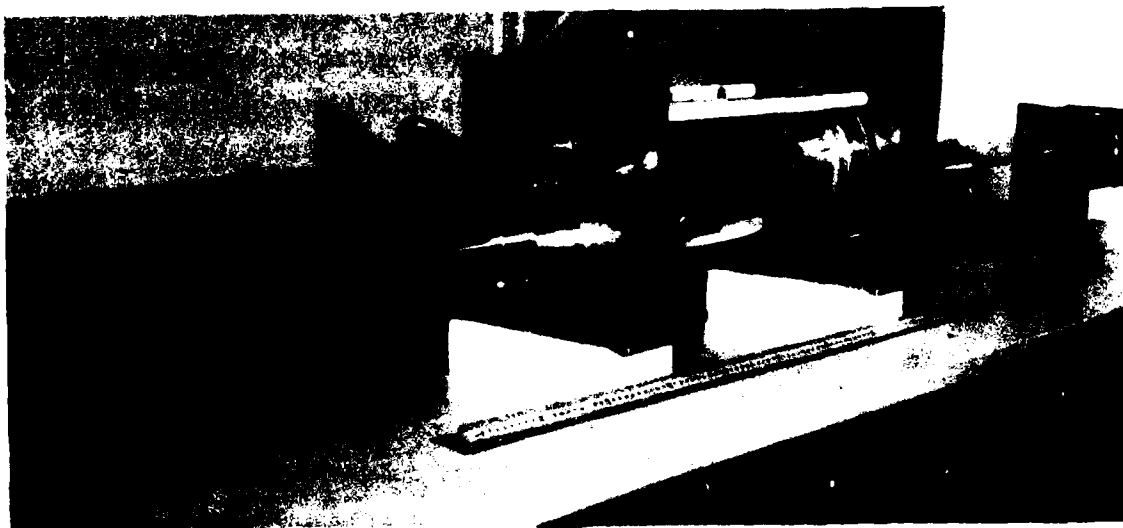


Figure 4 High PRF HgBr Laser with a HgBr₂ Reconstitution System

Since the active length of this laser was only 12 cm, the laser was always operated near its threshold which provided the most sensitive way for monitoring the degradation of the laser output. The output stability from pulse to pulse varied less than 15% while the long term stability changed less than 5% until $\sim 3 \times 10^7$ pulses. The life-test was temporarily interrupted twice because of thyatron failures. During the repair of the last thyatron failure, we modified the reconstitution system by slightly increasing the flow. Figure 5 shows the laser output as a function operating life. No sign of laser deterioration has been observed and the laser output remained constant at 392 μ J per pulse. A slight blackening on the preionizer rods indicated a material loss due to sputtering. Material loss from gold electrodes caused by sputtering was undetectable. The stainless steel end plates were placed purposely to generate some reaction products, so that one can test the effectiveness of the reconstitution system. After 3×10^7 pulses, we noticed some discoloration of the stainless steel plates but no sign of any effect on the HgBr laser performance. Aside from the thyatron, capacitors and some unexpected minor mechanical difficulties, the HgBr laser tube had no indications of any deterioration caused by chemical reactions. We firmly believe that a long-lived HgBr laser can be realized by using right material for the laser tube and installing a HgBr₂ reconstitution system to recover the bromine loss.

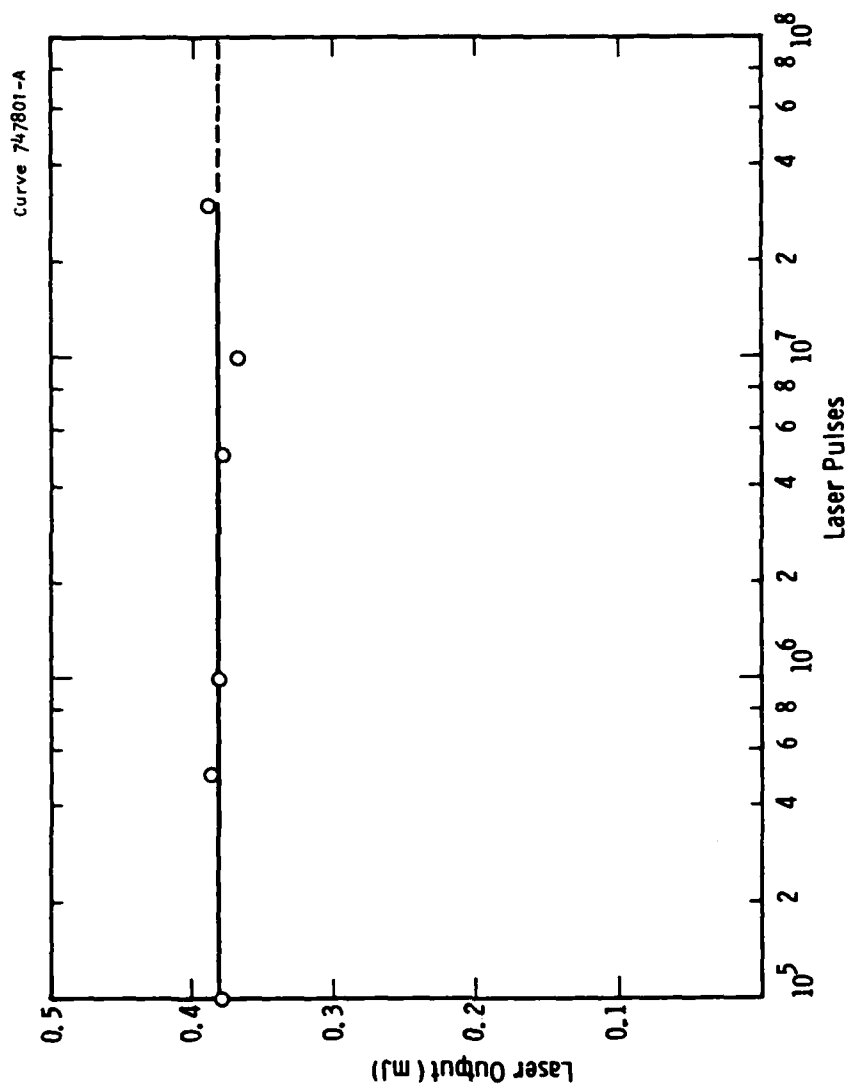


Figure 5 HgBr Laser Output vs. Operating Life

SUMMARY & RECOMMENDATIONS

The previous laser discharge study and laser lifetest indicated that a pinhole-free gold plated nickel was chemically inert to HgBr laser gases. Without any reconstitution system installed in a gold plated HgBr laser, the laser itself can last over 5×10^6 shots.³ For a larger laser system, pinhole-free gold plating becomes very difficult if not impossible; therefore, a reconstitution system for HgBr₂ was installed to take care of the pinhole problem. To exaggerate the pinhole in the gold plating, we purposely used an uncoated end-plate in a gold plated HgBr laser for lifetest and it has operated over 3×10^7 shots without any sign of laser deterioration. This test made us firmly believe that a gold-plated HgBr laser with a HgBr₂ recovery system can certainly last 10^8 shots and beyond. We did not test the system to failure in the present program; this would have to be done to determine the ultimate life of the HgBr laser system."

However, we are encouraged and optimistic about the lifetest result of our HgBr laser, and we believe that 10^{10} shots for HgBr lasers is obtainable. In addition, the same technique can be easily extended the the XeCl laser system. If one can install a HCl reconstitution system for XeCl laser instead of replacing HCl every so often,⁷ the whole laser system will be lighter, simpler and last longer than the present system.

This report was typed by Toni McElhaney.

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